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APPLIED SURFACE ANALYSIS WORKSHOP

John T. Grant

University of Dayton
Research Institute
Dayton, Ohio 45469

October 1979

TECHNICAL REPORT AFML-TR-79-4153

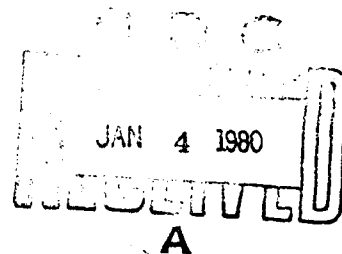
Final Report for Period 12 June 1979 - 15 June 1979

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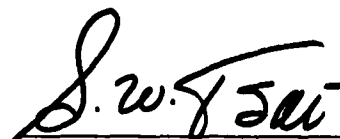
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This technical report has been reviewed and is approved for publication.



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Nonmetallic Materials Division



S. W. TSAI, Chief
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FOR THE COMMANDER



J. M. KELBLE, Chief
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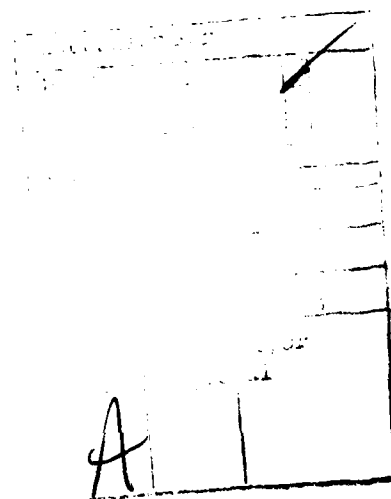
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FOREWORD

This report describes the Applied Surface Analysis Workshop held at the University of Dayton, 300 College Park Avenue, Dayton, Ohio 45469, on 13-15 June 1979, under Contract No. F33615-79-C-5130.

The Workshop was conducted by the University of Dayton Research Institute with Dr. John T. Grant of that organization and Dr. T. W. Haas of the Air Force Materials Laboratory as Co-Chairmen. The Workshop was supported by the Air Force Office of Scientific Research. This report was submitted in August 1979.



SECTION I

INTRODUCTION

A Workshop on Applied Surface Analysis was held at the University of Dayton, 13-15 June 1979. This workshop was held to meet a need, namely to show the transition between basic surface science research and applications of this research to areas of Air Force interest. Areas receiving special attention at this Workshop were adhesion, thermionic emission, thin film and solid state electronic device technology, and corrosion. Other topics discussed included energy conversion, coatings and catalysis. Approximately one hundred scientists active in the field of surface analysis participated in the Workshop. Five scientists presented invited papers at the Workshop. There were thirty-three contributed presentations.

SECTION II

WORKSHOP GOALS

Several symposia are held each year dealing with surface science research. These symposia cater chiefly to the academic community as most topics of discussion deal with basic research. For example, at the most recent national meeting of the American Vacuum Society, typical papers presented at the Surface Science sessions were: "Chemisorption of oxygen on the (110) surface of iridium," "Condensation and compression of argon monolayers on graphite," "Density of empty states in GeSe (001) and GeS (001)," and "Use of Fourier transforms for analyzing the extended fine structure above appearance potential thresholds." Such meetings have no clear provisions to include the results of applied surface studies, such as undertaken by most government laboratories and industry. While specialized workshops are held from time to time, such as the Tri-Service Cathode Workshop (held at the Naval Research Laboratory, Jan/Feb, 1978), there is no general meeting devoted primarily to those working in applied surface analysis. There are many areas in basic and applied surface science research of interest to the Air Force, such as the preparation of surfaces for adhesive bonding, the chemistry of corrosion products, electronic device technology, and thermionic emission. It was proposed, therefore, to show the transition between basic surface science research and applications of this research to areas of Air Force interest by bringing together those engaged in basic research and those engaged in applications of surface science research to discuss such applications of surface science, and to promote the maximum interaction between such workers.

To meet these goals a Workshop on Applied Surface Analysis was planned and organized by the University of Dayton, with Dr. John T. Grant of the University of Dayton and Dr. T. W. Haas of the Air Force Materials Laboratory as Co-Chairmen. Five invited speakers from universities and government laboratories were selected to cover specific areas of interest. These speakers and

their topics were:

- a) W. L. Baun, Air Force Materials Laboratory
"Applications of Surface Analysis Techniques to Studies of Adhesion."
- b) G. A. Haas, Naval Research Laboratory, "Recent Applications of Surface Analysis to the Understanding of Thermionic Emission."
- c) P. H. Holloway, University of Florida, "Characterization of Electronic Devices by Surface Analysis Techniques."
- d) R. L. Park, University of Maryland, "Surface Analysis on a Fixed Budget."
- e) C. J. Powell, National Bureau of Standards, "Recent Progress in Quantification of Surface Analysis Techniques."

Contributed papers on applied surface analysis were also solicited from the research community, resulting in thirty-three such papers being presented at the Workshop.

It was decided to publish as many of the papers as possible in an appropriate journal, thereby providing a permanent record of the work presented at the Workshop. The journal "Applications of Surface Science" was selected, and the journal editor was pleased to be able to publish such a proceedings. A majority of those presenting papers at the Workshop submitted manuscripts for peer review and eventual publication in the proceedings. It is hoped that the proceedings will be published and distributed to all attendees in the spring of 1980.

The Workshop was advertised through appropriate scientific societies, equipment manufacturers, scientific journals, and at other meetings. It was decided to hold the Workshop on the University of Dayton campus and to encourage attendees to stay in University apartments in order to provide an informal atmosphere and to optimize the interaction between attendees.

Two events were organized by the University and held in conjunction with the Workshop, namely a short course and a vendors' exhibit. The short course topic was "Techniques for Surface Analysis", and was held the day before the Workshop to provide an opportunity for attendees to learn the fundamentals of several surface analysis techniques, so that they could gain as much as possible from the Workshop presentations and in their own research. The vendors' exhibit provided an opportunity for attendees to learn about the commercial surface instrumentation that is currently available and what is planned for the future.

SECTION III
PARTICIPANTS

Approximately one hundred scientists active in the field of surface analysis attended the Workshop.

The list of participants follows.

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SECTION IV PROGRAM

The technical program was divided into six sessions, two being held each day of the three-day Workshop. There were five main sessions, and a short session on the last afternoon. Four sessions were devoted primarily to specific areas of interest, namely adhesion, thermionic emission, thin film and solid state electronic device technology, and corrosion. An invited speaker led off each of the main sessions.

The session on adhesion covered a number of different areas. W. L. Baun led off the session with a review of the applications of surface analysis techniques to studies of adhesion. Other papers presented were studies of paint adhesion loss in corrosion, the characterization of adherends for adhesive bonding applications, the bonding of polymers to metals, the oxidative degradation of polymer coatings and the characterization of graphite fibers used in structural epoxy matrix composite materials.

The session on thermionic emission began with a review by G. A. Haas on applications of surface analysis to the understanding of thermionic emission. The contributed papers dealt mainly with studies of dispenser cathodes.

P. H. Holloway reviewed the characterization of electronic materials and devices by surface analysis techniques. Other papers on device technology involved studies of the "blow" mechanism of programmable read only memories, the corrosion of gold-plated printed circuit board connectors, and studies of ion implants in gallium arsenide.

Some of the papers mentioned above dealt with corrosion. Other papers presented on this topic were the oxidation of brass, the oxidation of copper films on gold, the corrosion susceptibility of heat treated iron-chromium alloys, and the oxidation of an iron-nickel alloy.

The other two sessions covered papers of general interest, as well as papers on energy conversion, catalysis and non-vacuum surface analysis techniques.

The program organization and the abstracts of the papers presented at the Workshop follow.

SYMPOSIUM ON APPLIED SURFACE ANALYSIS

13 - 15 June 1979
University of Dayton

GENERAL INFORMATION

The Symposium on Applied Surface Analysis is being sponsored by the Air Force Office of Scientific Research. The Symposium will provide an opportunity for workers in all areas of surface characterization to meet and discuss applications of surface analysis. It is the aim of the symposium chairmen to attract participants from universities, and from Government, nonprofit and industrial laboratories to promote the maximum interaction between workers in different areas.

LOCATION AND DATES

The University of Dayton
300 College Park
Dayton, Ohio 45469
13-15 June 1979

Limousine service is available to downtown Dayton from Dayton International Airport every hour (20 minutes to the hour), for approximately \$4.50. Taxi service from downtown to the campus is approximately \$4. City bus service (#12) is available, leaving downtown Third and Main Streets approximately every 15 minutes. This bus passes the University apartment at 339 Irving Avenue and is \$.50. Apartment keys can be secured from the Apartment Caretaker/Manager upon arrival at the apartment. Checkout times on Friday, 15 June are 8:00-9:00 am, 12:00-1:00 pm, and 3:00-4:00 pm.

HEADQUARTERS

The Symposium headquarters will be adjacent to the O'Leary Auditorium located in Miriam Hall on the University of Dayton Campus. Emergency telephone messages can be taken at Area Code (513) 229-3118.

REGISTRATION

All symposium attendees should preregister by mail. Those preregistered may pick up their final programs, etc., on Tuesday evening between 7:00 and 10:00 pm in Apt. B, 339 Irving Avenue, if they desire. Symposium registration will also be held during the Symposium starting at 8:00 am on Wednesday, 13 June.

SESSIONS

All sessions will be held in O'Leary Auditorium located in Miriam Hall on the University Campus. The symposium will close at approximately 3:00 pm on Friday, 15 June.

PROCEEDINGS

The proceedings will be published in a special issue of "Applications of Surface Science". Manuscripts should be handed in at the Registration Desk.

RECEPTION

A reception will be held at 6:30 pm on Wednesday evening, 13 June at the University apartment complex, 339 Irving Avenue. This apartment complex is located close to the campus. Attendees are also invited to drop by Apartment B on Tuesday evening, 12 June between 7:00 and 10:00 pm for refreshments.

VENDORS EXHIBITS

Representatives from the major surface instrumentation and ultrahigh vacuum equipment manufacturers have been invited to participate in the Symposium. Table top exhibits will be presented by the vendors in Miriam Hall, Room 107. Representatives will be available to discuss your instrumentation needs. Exhibits will be open from 9:00 am to 5:00 pm on Wednesday and Thursday, and from 9:00 am to 12:00 noon on Friday.

ATTIRE

Dayton is known as one of Ohio's most progressive cities. Its 800 manufacturing plants distribute more than 1,000 products. There are many interesting places to visit while in the area. In June, the mean daytime temperature is 78°F to 81°F; the mean evening temperature is 55°F to 62°F. Since the temperature is quite variable, mid and lightweight dress is recommended.

SYMPOSIUM ADMINISTRATION

SYMPOSIUM SPONSOR

Air Force Office of Scientific Research
Bolling Air Force Base, DC

SYMPOSIUM CHAIRMEN

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AGENDA

WEDNESDAY MORNING, 13 JUNE 1979

SESSION A

Chairman: C. J. Powell
National Bureau of Standards

- 8:00 REGISTRATION
- 9:00 INTRODUCTORY REMARKS
- 9:20 A-1 R. L. Park (Invited)
University of Maryland
SURFACE ANALYSIS ON A FIXED BUDGET
- 10:10 A-2 C. T. Hovland
Perkin-Elmer
SOME APPLICATIONS OF SCANNING AUGER MICROSCOPY
- 10:30 A-3 L. L. Tongson*, A. S. Bhalla, L. E. Cross, and B. E. Knox
Pennsylvania State University
INVESTIGATION OF FERROELECTRIC SURFACES BY COMBINED
AES AND ISS TECHNIQUES
- 10:50 COFFEE BREAK
- 11:10 A-4 R. E. Chase, W. L. Gordon, and R. W. Hoffman
Case Western Reserve University
MEASUREMENT OF LOW ENERGY SECONDARY ELECTRON DISTRIBUTIONS
USING A DOUBLE PASS CYLINDRICAL MIRROR ANALYZER
- 11:30 A-5 P. C. Karalkar* and J. E. Nordman
University of Wisconsin
ESCA CHARACTERIZATION OF THE OXIDE TUNNELING BARRIERS IN
NIOBIUM BASED SUPERCONDUCTIVE TUNNEL JUNCTIONS
- 11:50 LUNCH

* Denotes presenting author.

WEDNESDAY AFTERNOON, 13 JUNE 1979

SESSION B

Chairman: P. H. Holloway
University of Florida

- 1:30 B-1 W. L. Baun (Invited)
Air Force Materials Laboratory
APPLICATIONS OF SURFACE ANALYSIS TECHNIQUES TO
STUDIES OF ADHESION
- 2:20 B-2 J. S. Hammond*, J. W. Holubka, and R. A. Dickie
Ford Motor Company
SURFACE ANALYTICAL STUDIES OF PAINT ADHESION LOSS IN CORROSION
- 2:40 B-3 D. E. Hanlin* and J. S. Solomon
University of Dayton Research Institute
AES AND SEM CHARACTERIZATION OF ANODIZED ALUMINUM
ALLOY ADHERENDS FOR ADHESIVE BONDING APPLICATION
- 3:00 COFFEE BREAK
- 3:20 B-4 W. J. van Ooij* and A. Kleinhesselink
Akzo Research
APPLICATION OF XPS TO THE STUDY OF POLYMER-METAL
INTERFACE PHENOMENA
- 3:40 B-5 A. W. Czanderna*
Solar Energy Research Institute, and
A. C. Miller
Alcoa Technical Center
ION SCATTERING PROFILES OF POLYPROPYLENE COATINGS ON $\text{CuO}_{0.67}^{18}$
FILMS BEFORE AND AFTER OXIDATIVE DEGRADATION OF
THE POLYMERS
- 4:00 B-6 G. E. Hammer*
Universal Energy Systems, and
L. T. Drzal
Air Force Materials Laboratory
GRAPHITE FIBER SURFACE ANALYSIS BY X-RAY PHOTOELECTRON
SPECTROSCOPY AND POLAR/DISPERSIVE FREE ENERGY MEASUREMENTS
- 4:20 B-7 P. P. Yaney* and R. J. Becker
University of Dayton
THE APPLICATION OF RAMAN SPECTROSCOPY TO THE STUDY OF
ADSORBED MOLECULES ON ALUMINA SURFACES
- 4:40 B-8 M. B. Chamberlain
McDonnell Douglas Research Laboratories
SOLID STATE REACTION OF Ti and SiC
- 5:00 ADJOURNMENT
- 6:30 RECEPTION
University Apartment, 339 Irving Avenue (First floor, Apt. B)

THURSDAY MORNING, 14 JUNE 1979

SESSION C

Chairman: R. L. Park
University of Maryland

- 9:00 C-1 G. A. Haas (Invited)
Naval Research Laboratory
RECENT APPLICATIONS OF SURFACE ANALYSIS TO THE
UNDERSTANDING OF THERMIONIC EMISSION
- 9:50 C-2 T. N. Wittberg and C. G. Pantano*
University of Dayton Research Institute
SURFACE CHARACTERIZATION OF THE MEDICUS NICKEL-
MATRIX CATHODE
- 10:10 C-3 W. V. Lampert*, B. C. Lamartine, and T. W. Haas
Air Force Materials Laboratory
X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF THE ACTIVATION
MECHANISM OF THE DISPENSER CATHODE
- 10:30 COFFEE BREAK
- 10:50 C-4 D. L. Jones
Tektronix, Inc., and
P. R. Davis
Oregon Graduate Center
SURFACE STUDIES OF IMPREGNATED DISPENSER CATHODE ACTIVATION
- 11:10 C-5 W. L. Baun
Air Force Materials Laboratory
CHARACTERIZATION OF TUNGSTEN DISPENSER CATHODES USING ISS
AND SIMS
- 11:30 C-6 G. R. Sparrow
3M Center
STUDIES OF SURFACE CONTAMINANTS USING ISS/SIMS: GLASS
AND SEMICONDUCTOR
- 11:50 C-7 N. C. Fernelius
University of Dayton Research Institute
PHOTOACOUSTIC SPECTROSCOPY STUDIES ON OPTICAL COATINGS
AND MATERIALS
- 12:10 LUNCH

THURSDAY AFTERNOON, 14 JUNE 1979

SESSION D

Chairman: R. W. Hoffman
Case Western Reserve University

- 1:30 D-1 P. H. Holloway* (Invited)
University of Florida, and
G. E. McGuire
Tektronix, Inc.
CHARACTERIZATION OF ELECTRONIC MATERIALS AND DEVICES BY
SURFACE ANALYSIS TECHNIQUES
- 2:20 D-2 Y. S. Park*, W. M. Theis
Air Force Avionics Laboratory, and
J. T. Grant
University of Dayton Research Institute
CHARACTERIZATION OF ION IMPLANTS IN GaAs BY AES and GDOS
- 2:40 D-3 J. S. Murday and E. G. Shafrin*
Naval Research Laboratory
J. D. Guttenplan, and L. N. Hashimoto
Rockwell International
CHEMICAL CORROSION CONTROL FOR GOLD-PLATED PCB CONNECTORS
- 3:00 COFFEE BREAK
- 3:20 D-4 C. L. Strecker
Air Force Materials Laboratory
W. E. Moddeman*
University of Dayton Research Institute, and
G. R. Sparrow
3M Company
ION SCATTERING SURFACE EXAMINATIONS OF CALCIUM FLUORIDE
LASER WINDOW MATERIALS
- 3:40 D-5 T. F. Schaaf
Western Electric Company
SURFACE SILVER ON GOLD ELECTRODEPOSITS
- 4:00 D-6 S. Maroie*, G. Debras, R. Caudano, and J. Verbist
Facultes Universitaires
A STUDY OF THE OXIDATION OF α AND β BRASS BY PROMPT NUCLEAR
REACTIONS AND RUTHERFORD BACKSCATTERING
- 4:20 D-7 A. C. Miller*
Alcoa Technical Center, and
A. W. Czanderna
Solar Energy Research Institute
ION SCATTERING CHARACTERIZATION OF THE OXIDATION OF THIN
COPPER FILMS ON GOLD SUBSTRATES

(continued on the following page)

THURSDAY AFTERNOON CONTINUED

4:40 D-8 H. G. Tompkins* and M. R. Pinnel
Bell Telephone Laboratories
ON THE RATE CONTROLLING STEP OF COPPER DIFFUSION/OXIDATION
THROUGH GOLD

5:00 ADJOURNMENT

FRIDAY MORNING, 15 JUNE 1979

SESSION E

Chairman: W. L. Baun
Air Force Materials Laboratory

- 9:00 E-1 C. J. Powell (Invited)
National Bureau of Standards
RECENT PROGRESS IN QUANTIFICATION OF SURFACE
ANALYSIS TECHNIQUES
- 9:50 E-2 A. Rengan* and W. E. Moddeman
University of Dayton Research Institute
P. S. Wang, and L. D. Haws
Monsanto Research Corporation
EFFECT OF SURFACE PLASMON EXCITATION ON ALUMINUM OXIDE
THICKNESS CALCULATION IN Al/Cu_2O THERMITE APPLICATIONS
- 10:10 E-3 J. R. Naegele*, L. Manes, and J. C. Spirlet
European Institute for Transuranium Elements
SURFACE STUDIES BY PHOTOEMISSION OF LAVES-PHASES $UA1_2$
AND UCo_2
- 10:30 COFFEE BREAK
- 11:10 E-4 R. G. Hart and G. W. Simmons
Lehigh University
AES STUDIES OF THE INFLUENCE OF VACUUM AND HYDROGEN
ANNEALING ON THE SURFACE COMPOSITION OF 2-1/4 Cr - 1 Mo
(ASTM A542) STEEL
- 11:30 E-5 D. Buczek, R. McDonald, and S. Sastri
The Gillette Company
A STUDY OF OXIDE COMPOSITION AND CORROSION SUSCEPTIBILITY
OF A HEAT TREATED Fe - Cr ALLOY USING AUGER ELECTRON
SPECTROSCOPY
- 11:50 E-6 T. N. Wittberg*, J. R. Hoenigman, W. E. Moddeman
University of Dayton Research Institute, and
R. L. Salerno
Monsanto Research Corporation
STUDIES OF OXIDE FILMS ON IRON-NICKEL ALLOY 52 USING AES
- 12:10 LUNCH

FRIDAY AFTERNOON, 15 JUNE 1979

SESSION F

Chairman: W. E. Moddeman
University of Dayton Research Institute

- 1:30 F-1 J. A. Taylor* and C. D. Wagner
Perkin-Elmer
THE USE OF BREMSSTRAHLUNG RADIATION TO PRODUCE AUGER
LINES INACCESSIBLE TO MgK_{α} AND AlK_{α} X-RAYS
- 1:50 F-2 Y. E. Strausser*
Hewlett-Packard Laboratories, and
R. G. Musket
Kevex Corporation
THE USE OF ENERGY DISPERSIVE X-RAY SPECTROMETRY IN CONJUNCTION
WITH AUGER ELECTRON SPECTROSCOPY FOR THIN FILM ANALYSIS
- 2:10 F-3 B. C. Lamartine*, T. W. Haas
Air Force Materials Laboratory, and
J. S. Solomon
University of Dayton Research Institute
ELECTRON SPECTROSCOPY OF $TiD_{0.9}$ and TiH_x SURFACES
- 2:30 F-4 R. G. Keil
University of Dayton
THE FORMATION OF THIN UNIFORM INSULATING FILMS FOR
INELASTIC ELECTRON TUNNELING SPECTROSCOPY
- 2:50 ADJOURNMENT

Surface Analysis on a Fixed Budget

Robert L. Park

Department of Physics and Astronomy

University of Maryland

The history of surface physics is more a record of the development of new analytical techniques for the characterization of surfaces, than of the development of great unifying theories. The most basic requirements in this characterization are to identify the chemical constituents of the surface region, and to determine their structural arrangement. Progress in chemical identification has been rapid since the introduction of Auger electron spectroscopy (AES) just a decade ago. Surface crystallography, on the other hand, began more than half a century ago with the discovery of low energy electron diffraction (LEED), but the complexity of LEED analysis has limited its use to a few relatively simple structures. Using extended appearance potential fine structure (EAPFS) techniques, however, it is now possible to extract structural information from even highly disordered surfaces. As with AES, EAPFS requires only an inexpensive electron source for excitation.

A-1

Wednesday - 9:20 am

SOME APPLICATIONS OF SCANNING AUGER MICROSCOPY

by

C. T. Hovland
Perkin Elmer, Physical Electronics Division
6509 Flying Cloud Drive
Eden Prairie, MN 55344

Developments in scanning Auger microscopy resulting in less than 500Å spatial resolution of the primary electron beam are important for analysis of high technology microelectronics devices. For device geometrics with submicrometer metallizations and high surface to volume ratios, the small analysis volume of Auger microscopy is a key factor in characterization and problem solving.

Scanning Auger microanalysis of nickel-chrome linked programmable read only memories with less than 200Å thick metallization has been conducted. This analysis has resulted in improved understanding of the "blow" mechanism in programmed devices.

A-2

Wednesday - 10:10 am

INVESTIGATION OF FERROELECTRIC SURFACES BY COMBINED
AES AND ISS TECHNIQUES. L.L. Tongson, A.S. Bhalla,
L.E. Cross and B.E. Knox. Materials Research Labora-
tory, The Pennsylvania State University, University
Park, PA 16802.

Basic studies of ferroelectric crystal surfaces are of interest and importance for several reasons. First, the ferroelectrics are a subgroup of the much larger family of polar crystals. In all these materials the surface properties will be markedly modified by the orientation of the electric polarization vector with respect to the crystal surface. In ferroelectrics, because of the domain structure and switching possibility, these effects can be studied in a simple and controlled manner. Second, in many ferroelectrics there is considerable indirect evidence from dielectric and nonlinear dielectric measurements of the existence of a "modified" surface region. Both physical and chemical models have been proposed to explain observed data and there is an urgent need for more detailed information about the crystal surfaces to decide the validity of these hypotheses.

In the present study, quasi-simultaneous Auger electron and ion scattering spectrometries were used to determine the chemical nature of pristine and chemically reacted surfaces of barium titanate and gadolinium molybdate crystals. Data are presented and discussed in relation to secondary features of the AES and ISS spectra that convey (1) chemical bonding information of the constituent elements and (2) the type of the emergent polarization in essentially single domain faces. Effects of ion beam of various inert gases on the ferroelectric surfaces are also discussed briefly.

A-3

Wednesday - 10:30 am

Measurement of Low Energy Secondary Electron

Distributions Using a Double Pass

Cylindrical Mirror Analyzer^{*}

R.E. Chase, W.L. Gordon, R.W. Hoffman

Department of Physics

Case Western Reserve University, Cleveland, Ohio 44106

A commercial double pass cylindrical mirror analyzer (CMA) has been adapted to measure the low energy portion (< 80 eV) of the secondary electron distribution. Under normal operating conditions for the CMA, the presence of stray electric and magnetic fields within the CMA plus the poor electron multiplier response at low energy prevent quantitative measurements in the region where the secondary electron distribution reaches its maximum (< 5 eV). To circumvent this problem, we apply an accelerating potential (< 100 volts) to the "retarding" grid at the entrance of the CMA. The accelerating potential translates the secondary electron distribution to high enough energies that the theoretical response of the CMA ($EN(E)$) is valid, but low enough to still give reasonable resolution. Moreover, we are able to separate out the small secondary electron peak due to the first (grounded) grid by applying a small accelerating potential to the sample. This use of the CMA for measuring secondary electron distributions allows the surface to be characterized by AES before and after measurement. We present results for clean copper and silver. In the $\log N(E)$ versus $\log E$ format, we observe the linearized cascade with Auger peaks clearly visible.

^{*}Research supported by NASA through grant No. NSG-3197

A-4

Wednesday - 11:10 am

ESCA CHARACTERIZATION OF THE OXIDE TUNNELING BARRIERS
IN NIOBIUM BASED SUPERCONDUCTIVE TUNNEL JUNCTIONS.*

P.C. KARALKAR and J.E. NORDMAN, UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN 53706. -- Volt-ampere characteristics of niobium based superconductive tunnel junctions (e.g. niobium-niobium oxide-lead) commonly exhibit excess quasiparticle currents for voltages less than the sum of the half-gap values for the superconductors on either side of the tunneling barrier. The presence of a thin layer of niobium monoxide in the interface between the Nb electrode and the Nb₂O₅ tunneling barrier is believed by many to be responsible for the excess currents.¹ However, direct detection of niobium monoxide in the extremely thin (≈ 30 Å) tunneling barriers has not been reported to date. We have used x-ray photoelectron spectroscopy (ESCA) to study the niobium oxide tunneling barriers produced by an rf glow discharge oxidation technique.² Photoelectron spectra obtained from known samples of Nb, NbO, NbO₂, and Nb₂O₅ were used for comparison. Our results clearly showed that the thin oxide films contain detectable amounts of NbO and that the amount can be changed by changing the oxidation procedure. We have also studied Nb-Nb oxide-Pb superconductive tunnel junctions fabricated by using the oxidation procedures identical to those used for preparing ESCA samples. Our study, for the first time, clearly demonstrates that large excess currents in niobium based junctions are associated with the presence of large amounts of niobium monoxide in the junction barrier.

¹ B. Robinson, T. H. Geballe, and J. M. Rowell, Superconductivity in d- and f-band metals, ed. by D. H. Douglass (Plenum Press, New York, 1976), p. 381.

² P. C. Karulkar and J. E. Nordman, Bull. Am. Phys. Soc. 24, 299 (1979).

* Partially supported by NSF Grant ENG 74-24227.

APPLICATIONS OF SURFACE ANALYSIS TECHNIQUES
TO STUDIES OF ADHESION

W. L. Baun

Mechanics & Surface Interactions Br. (MBM)
Air Force Materials Laboratory
Wright-Patterson AFB, Ohio 45433

The question is often asked, "Which is the best surface chemistry tool for research on adhesive bonding?" This question is difficult to answer because it depends on the aspect of adhesion which is being studied. Often a combination of instruments must be used to take advantage of the strong points of each. In metal-to-metal bonding there are many facets of adhesive/adherend interaction which may be studied. Elemental characterization of adherends, especially when composition with depth is desired, is often best accomplished with Auger Electron Spectroscopy (AES). When information on chemical bonding is required, X-ray Excited Photoelectron Spectroscopy (XEPS) is the choice of most workers. Extremely thin layers of material (when first surface sensitivity is needed) requires Ion Scattering Spectrometry (ISS). The extremely high sensitivity of Secondary Ion Mass Spectrometry (SIMS) to many elements important in adhesive bonding makes this technique useful, especially coupled with other methods, such as ISS and AES. Modern surface analysis along with Scanning Electron Microscopy (SEM) provides information on failure surfaces to allow unequivocal determination of locus of failure. Problems such as charging and decomposition under the probing beam are encountered when characterizing the part of the failure surfaces containing the adhesive.

Although original surfaces and failure surfaces following testing are relatively routinely analyzed, the characterization of the intact bond is not so easy. The interphase region between adherend and adhesive is smaller than the probe, exhibits charging and is unstable. Although no one technique adequately characterizes the bond interphase region, the SEM, the AES microprobe, and special techniques using Transmission Electron Microscopy (TEM), may be used to gain some information about the bond. The more fundamental study of the interaction of polymers and polymer precursors with metals and alloys is carried out by surface energetics measurements, infrared and Raman spectrometries, XEPS and electron tunneling spectroscopy.

Key words: Surface characterization, adhesive bonding, adherend, adhesive, AES, XEPS, ISS, SIMS, SEM.

B-1

Wednesday - 1:30 pm

SURFACE ANALYTICAL STUDIES OF PAINT ADHESION LOSS IN CORROSION. J. S. Hammond, J. W. Holubka and R. A. Dickie, Ford Motor Company, Engineering and Research Staff, P. O. Box 2053, Dearborn, Michigan 48121.

Paint adhesion is often disrupted adjacent to sites of corrosion on painted steel. We have employed X-ray photoelectron spectroscopy to study the interfacial chemistry of corrosion-induced adhesion loss. In the case of an epoxy-ester-based coating applied to bare steel, the adhesion loss attributable to corrosion-generated hydroxide ion results from degradation of polymer near the metal-polymer interface. This work has been extended to saponification-resistant epoxy-amine based coatings formulated with and without an organo-phosphate additive and applied to bare steel. Adhesion failure induced by corrosion-generated hydroxide is again associated with coating degradation near the interface. As expected, the rate of failure is much slower with saponification-resistant resin formulations.

Results on the epoxy-ester-based coating applied over an inorganic conversion coating are also reported; there is evidence of degradation of the paint resin and also of a change in surface composition of the conversion coating. The locus of failure is at or very near the organic-inorganic coating interface.

B-2

Wednesday - 2:20 pm

AES and SEM Characterization of Anodized Aluminum
Alloy Adherends for Adhesive Bonding Application

by

D. E. Hanlin and J. S. Solomon
University of Dayton Research Institute
Dayton, Ohio 45469

Anodization is one of the primary surface treatments to aluminum alloy panels which are to be adhesively bonded. An adhesively bonded structure of aluminum with an anodic oxide surface offers superior performance in terms of strength and durability over chemically etched surfaces. The anodization process involves a number of variables, all of which have some effect on the anodic oxide characteristics. These include: electrolyte pH, temperature, anodization, time, and applied potential.

AES and SEM were used to determine the effects of some of the anodization variables on oxide structure and chemistry. Elemental sputter profiles through the anodic oxide films provided insights as to the role of alloying constituents during anodization and their effects on oxide thickness. Pore size and orientation were characterized by scanning transmission microscopy (STEM).

The results of the study show that both techniques offer important information; however, only when their individual results are combined can one begin to thoroughly assess the influence of the individual anodization parameters on the anodic oxide character.

B-3

Wednesday - 2:40 pm

APPLICATION OF XPS TO THE STUDY OF POLYMER-METAL INTERFACE PHENOMENA

W.J. van Doij and A.Kleinhesselink, Akzo Research,
Corporate Research Department Arnhem, The Netherlands

XPS has been used to identify the mechanism of adhesion and adhesion failure of metals to polymers, e.g. sulfur-vulcanized natural rubber. Thin slabs of rubber were cured in contact with a series of metals and alloys. The rubber-metal interface was analyzed and the results were compared with the strength of the bond. High bond strengths exceeding the rubber tear strength are obtained only if an interfacial film of sulfidic reaction products is formed which becomes an integral part of the bond. Neither very slow nor very high rates of sulfidization lead to optimum bond strengths. It is postulated that metal sulfidization affects the rubber chemistry leading to an increased crosslink density in the rubber surface layers. XPS analyses of cured rubber surfaces have provided evidence to support this view.

Various types of adhesion failure have been observed. CuNi alloys do not bond well because of poor adhesion between the NiS and Cu_xS layers of the interfacial film. The very strong bond to CuZn alloys fails during aging in steam as a result of partial dezincification of the unreacted brass leading to a Weak Boundary Layer of ZnO and Cu_xS . Minor changes in compound formulation lead to drastic differences with respect to aged adhesion of CuZn alloys, however. Good compounds form homogeneous sulfide films consisting of ZnS and Cu_xS which passivate the brass. Poor compounds form irregular sulfide films containing ZnO which do not passivate the metal. Addition of a few per cent of Ni to CuZn alloys leads to a much improved aged adhesion retention. XPS analyses of the interface suggest that this is due to an inhibition of the brass dezincification reaction which suppresses interfacial film growth.

B-4

Wednesday - 3:20 pm

ION SCATTERING PROFILES OF POLYPROPYLENE COATINGS ON
 $\text{CuO}_{0.67}^{18}$ FILMS BEFORE AND AFTER OXIDATIVE DEGRADATION
OF THE POLYMER*

A. W. Czanderna, Solar Energy Research Institute, Golden Colorado
and

A. C. Miller, Alcoa Technical Center, Alcoa, PA

Polymers are known to degrade oxidatively in the presence of copper and its salts. A basic question is to determine the role of the polymer copper oxide interface in the catalyzed oxidative degradation of polypropylene.

Copper films were deposited onto glass substrates and oxidized partially or completely to $\text{CuO}_{0.67}$ in oxygen-16 or oxygen-18. The 44 nm thick oxide films were overlaid with 40 to 110 nm of polypropylene (pp) by a dip coating process. The pp/ $\text{CuO}_{0.67}$ /glass samples were heated in oxygen-16 at temperatures of 90, 100, 110 and 120° in the presence and absence of getters for the product gases. ISS depth profiles were obtained for deposited copper films, partially and completely oxidized films (both labeled and unlabeled) and for undegraded and oxidatively degraded polymer/oxide sandwiches.

Analysis of the copper oxides formed in oxygen-16 and oxygen-18 showed the expected separation of the maxima of 0.03 E/ E_0 in the energy loss spectrum. For all 16-18 combinations, the sum of the peak intensities is the same as for the intensity of oxygen-16 in $\text{CuO}_{0.67}$.

In the presence of getters, the copper oxide films is reduced by the polypropylene but is not reoxidized, leaving the copper oxide film nearly all reduced to copper. The O^{16}/O^{18} ratio in the unreduced oxide remained unchanged from the original ratio. The degraded polypropylene was more difficult to sputter and the profile showed copper was present throughout the polymer thickness.

In the absence of getters, the copper oxide film is reduced but reoxidized by the oxygen ambient used during the oxidative degradation. The O^{16}/O^{18} ratio in the oxide after degradation exhibits a marked increase in oxygen-16. Extensive oxidation of the polypropylene is evident from the O^{16} signal in the polymer and, again, copper ions are found distributed throughout the polypropylene.

The results show that reduction of the copper oxide by the polymer is part of the mechanisms by which copper catalyzes polypropylene degradation. In the case corresponding to normal environments (no getters), partial reoxidation of the copper also occurs, so a reduction-reoxidation cycle at the copper/polymer interface is suggested.

* Most of this work was carried out at Clarkson College, Potsdam, N.Y.

B-5

Wednesday - 3:40 pm

GRAPHITE FIBER SURFACE ANALYSIS BY X-RAY PHOTOELECTRON
SPECTROSCOPY AND POLAR/DISPERSIVE FREE ENERGY MEASUREMENTS

G.E. HAMMER
UNIVERSAL ENERGY SYSTEMS, INC., DAYTON, OHIO 45432, USA
AND

L.T. DRZAL
AIR FORCE MATERIALS LABORATORY, WPAFB, OHIO 45433, USA

Graphite fibers of less than 10 microns in diameter are used as the reinforcing agents in structural epoxy matrix composite materials. Their efficiency in reinforcing is determined to a large extent by their degree of bonding to the epoxy. Commercial surface treatments maximize this adhesion without understanding the molecular interactions involved. The purpose of this work has been to relate the surface composition of commercial treated and untreated fibers as measured by XPS in vacuum to the surface free energy of these fibers measured in air.

Hercules A and HM fibers, treated and untreated, have been studied using X-ray photoelectron spectroscopy (XPS) and contact angle measurements before and after a 300°C vacuum heat treatment. XPS spectra indicated multiple chemical states of carbon and oxygen and a reduction in the high energy binding state of carbon on the treated A fiber after vacuum heat treatment. Elemental surface concentrations have been calculated using corrected XPS peak areas. Contact angles were measured on these same fibers using a micro-Wilhelmy technique which incorporated eight liquids having a wide range of polar to dispersive free energy ratios. Determination of the fiber surface free energies and the proportions due to polar and dispersive components was made.

Good correlation was found between the oxygen concentration as measured by XPS and the change in polar/dispersive ratios for the fibers with surface treatments.

B-6

Wednesday - 4:00 pm

The Application of Raman Spectroscopy
to the Study of Adsorbed Molecules on Alumina Surfaces

Perry Pappas Yaney and Roger J. Becker
Department of Physics
University of Dayton

Surfaces of Alumina powders from a variety of suppliers have been studied using the Raman spectra recorded in air by excitation of the powder surface with a 532 nm pulsed laser beam. The results of these studies which were largely concerned with the amount and character of adsorbed H_2O and CO_2 on the "as received" materials will be presented. These powders were being used in the manufacture of ceramic supports; however, the area of study also relates to catalytic activity of the powders. In particular, studies of benzene adsorbed on alumina which related to bifunctional catalysts will also be presented. Other studies of composite "green" materials used in manufacturing processes which include alumina will be described. The current status of the surface Raman technique including features and limitations will be presented.

B-7

Wednesday - 4:20 pm

Solid-State Reaction of Ti and SiC*

M. B. Chamberlain
McDonnell Douglas Research Laboratories
St. Louis, Missouri 63166

The solid-state reaction of rf sputter-deposited, 0.4- μ m-thick Ti films on polished and etched 6H-polytype SiC (002) was investigated at 825-875 K. Reaction couples isothermally annealed for 16 h at 825 and 875 K were compositionally analyzed by combining Auger electron spectroscopy and Ar-ion sputtering. The annealed specimens were interdiffused, and Ti-Si intermetallics or Ti-C compounds were not observed. The interdiffusion kinetics in this system are similar to those¹ in rf sputtered Ni films on (111) and (100) Si.

¹G. L. P. Berning and L. L. Levenson, Thin Solid Films 55, 473 (1978).

*This research was conducted under the McDonnell Douglas Independent Research and Development program.

Recent Applications of Surface Analysis to the Understanding of Thermionic Emission

G. A. Haas

Naval Research Laboratory, Washington, DC 20375

The physical property of a solid which limits the number of electrons that are allowed to leave when the solid is heated is called the work function and the number of electrons leaving per unit time is called the thermionic emission.

The work function of a solid is determined largely by the outermost atomic configuration and as such, a study attempting to correlate work function with atomic composition requires the use of surface analysis techniques that are truly surface sensitive, that is, capable of observing even small changes in the first atomic layer. These surface compositional techniques must then be combined with various new surface electronic techniques so that a correlation can be made between the compositional and electronic properties of the solid and the mechanisms by which one affects the other. The class of solids which are of great interest in the electron device area are the semiconductors composed of the alkaline earth oxides, particularly BaO, because of the widespread use of these in electron emission applications. Emphasis in this discussion will therefore be heavily weighted toward examples of how some of these various different techniques are being applied to the understanding of the surface properties of these alkaline earth oxides.

The compositional techniques involve Auger electron spectroscopy (AES) and ion scattering spectroscopy (ISS) while the electronic techniques are scanning low energy electron probing (SLEEP) and low energy electron reflections (LEER). The compositional techniques are commercially available models while the electronic techniques were developed at NRL. SLEEP uses a scanning beam of incident electrons in the retarding field region to measure the work function of different spots. 30,000 such work function determinations are made in the 3 seconds required for one scan; the results are then displayed on a CRT in distribution-plot form. A TV presentation of the work function topograph is also available. The LEER system uses low energy incident electrons on a single crystal surface and analyzes the interaction of the electron wavelength with the lattice periodicity. This allows the separation of the work function into its two components, namely the position of the Fermi level with respect to the bottom of the conduction band and the position of the vacuum level with respect to the bottom of the conduction band. These two properties are often referred to as the "internal work function" and the "electron affinity, respectively. Examples will be given showing correlation from the combined use of these various techniques.

C-1

Thursday - 9:00 am

Surface Characterization of the Medicus Nickel-Matrix Cathode

T. N. Wittberg and C. G. Pantano
University of Dayton Research Institute
Dayton, Ohio 45469

Auger electron spectroscopy (AES) has been utilized to monitor the surface compositional behavior of the Medicus nickel-matrix cathode during activation and emission. Both the cathode surface and the anode from a closely spaced diode arrangement in the AES system were analyzed. Sulfur and manganese, which are trace impurities in the Ni matrix, were found to segregate on the cathode and anode surfaces, respectively, during activation. Although this cathode is reported to provide exceedingly homogeneous emission, scanning Auger micrographs reveal that compositional inhomogeneities exist on the 3-5 μ m scale. Attempts to quantify the compositional variations required extensive calibration using a range of oxide cathode compositions. In addition to providing a calibration for the measured Auger signals, the Auger analysis of oxide standards revealed significant electron beam desorption effects. The surface compositions calculated for a number of cathodes are correlated with the thermionic emission properties.

C-2

Thursday - 9:50 am

X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF THE ACTIVATION
MECHANISM OF THE DISPENSER CATHODE

by

W. V. Lampert
B. C. Lamartine

and

T. W. Haas

Air Force Materials Laboratory (MBM)
Wright-Patterson Air Force Base, OH 45433

X-ray photoelectron (XPS) and Auger electron (AES) spectroscopic analyses of the chemical changes taking place on commonly used dispenser cathodes during activation have been completed. The chemical composition and work-function changes of the cathodes were correlated at various stages of activation. The XPS shifts of the Ba 3d and 4p, O1s, and W4f binding energies suggest three distinct phases of activation: (1) Below about 500°C, the cathode appears to desorb common contaminants; (2) At about 800°C, metallic tungsten and barium states are formed; and (3) At operating temperatures, metallic tungsten remains, and the barium suffers some limited oxidation. Comparison to standard spectra by spectrum subtraction techniques failed to show more than one distinct barium species above 800°C. A discussion will be given for these results in terms of existing models of cathode activation and operation.

C-3

Thursday - 10:10 am

40

SURFACE STUDIES OF IMPREGNATED
DISPENSER CATHODE ACTIVATION

DOUGLAS L. JONES
Tektronix, Inc.
P.O. Box 500
Beaverton, Oregon 97077

PAUL R. DAVIS
Oregon Graduate Center
19600 N.W. Walker Road
Beaverton, Oregon 97005

The type M Impregnated Dispenser Cathode (IDC) has been studied using various surface analytical techniques with emphasis on the relation of emission performance to surface conditions. The Os/Ru coating of the M cathode has a columnar structure which appears to provide a more favorable geometry for supplying a uniform low work function coating to the surface of an IDC.¹ A comparison of the Field Emission Retarding Potential (FERP) and thermionic (Richardson) work functions of various IDC's confirms this. During the activation process Ba and BaO diffuse out from the pore regions to a diffusion length limited by evaporation. The total vaporization flux of Ba + BaO during initial operation is studied as a function of cathode type and pretreatments. Maintaining a low evaporation current while achieving a high emission current is desirable for many electron tube applications. The ratio of emission to evaporation current can be a useful figure of merit in evaluating electron emitters. X-ray Photoelectron Spectroscopy (XPS) studies show a reduction of the surface tungsten oxide to free tungsten as the Ba outdiffuses during activation. The Ba also changes binding state during this process.

¹ Jones, D., McNeely, D., Swanson, L.W., Applications of Surface Science 2, 232 (1979).

CHARACTERIZATION OF TUNGSTEN DISPENSER CATHODES
USING ISS AND SIMS

W. L. Baun

Mechanics and Surface Interactions Br. (MBM)
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Ion Scattering Spectrometry (ISS) and Secondary Ion Mass Spectrometry (SIMS) are used to characterize surface chemistry of barium-activated tungsten dispenser cathodes. Experiments were carried out at room temperature and at temperatures in which emission was occurring from the cathode structures. It was found that when the cathode structure was heated to a point at which electron emission began, barium concentration at the surface also increased. At that temperature, the barium is generated, transported through the porous tungsten matrix, and spread over the emitting tungsten surface. Apparently, sputtering rates from these barium rich surfaces were very high and when ion beams were used at 1000 volts or more, the sputtering rate was sufficiently large to suggest that incomplete coverage of barium existed. When very low ion beam voltages were used (in the neighborhood of 200-300 volts), and beam rastering techniques were employed, then results showed that the surfaces following activation were completely covered by barium.

C-5

Thursday - 11:10 am

STUDIES OF SURFACE CONTAMINANTS USING ISS/SIMS:
GLASS AND SEMICONDUCTOR

by

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The role of contaminants in the research and development of many new devices has been painfully emphasized during the past decade. Fortunately in many cases contamination is highly segregated in the outer surface, frequently in merely the outer few monolayers. Often it is simply satisfactory to have the analytical capability to answer the question: Is the surface of a particular material contaminated? This can be immediately followed by the question: To what degree is it contaminated? (quantitative aspects).

A systematic approach has been developed in our laboratories to routinely monitor surface contaminants on numerous Si wafers and glasses. The trace contaminants generally occurring on the outer few Å of most semiconductors are Na and K. In addition trace levels of Li, Ca, Ti, Cu, and Cr are observed and occasionally Mo. Trace high mass elements are monitored by ISS. Semiquantitative results will be presented.

The amount and depth surface organic material is monitored by low energy, low density ISS using ^3He . In addition very precise measurements of O/Si ratios by ISS are used to monitor the thickness and stoichiometry of SiO_2 layers. The same routine procedure has been used to monitor the degree and depth of oxygen penetration in thin Si_3N_4 passivation layers.

Depth profiles of trace dopants used in many common semiconductor materials can be monitored either by ISS or SIMS. B, P, S, and Cl are analyzed by SIMS and Ge, As, Se, Sb, and Te are monitored by ISS depending upon the substrate.

Numerous applications will be reviewed along with guidelines summarizing some estimated detection limits and some of the instrumental parameters utilized.

C-6

Thursday - 11:30 am

43

Photoacoustic Spectroscopy Studies on
Optical Coatings and Materials*

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Photoacoustic spectroscopy (PAS) is a recently revived technique which yields spectra similar to optical absorption spectra. Its main advantage is that spectra are obtainable on a variety of sample types which do not yield useful results by more conventional optical techniques. Examples of three of these sample types will be presented. Most of the data presented will be on visible wavelength optical absorption edges in semiconducting materials used in making optical coatings.

Powdered samples have too much scattering for useful optical transmission spectra, yet provide good PAS results. An example will be shown of the edge in rutile and anatase TiO_2 . Also examples of T&I powders, some with absorbed I_2 gas, will be given.

Highly absorbing samples yield PAS spectra with little sample preparation. An example of this is the spectrum from a slab of BiI_3 .

PAS spectra of thin films on a transparent substrate yield spectra without the multiple reflection interference fringes seen on conventional spectrometers. Some examples of T&I coatings on KCl and ZnSe coatings of several thicknesses on CaF_2 will be shown. Interpreting the resulting absorption edges gives information on the films' crystal structure and stoichiometry.

*This work was supported by the Air Force Office of Scientific Research and the Air Force Materials Laboratory, WPAFB, OH 45433.

Characterization of Electronic Materials
and Devices by Surface Analysis Techniques

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and

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Although analytical techniques sensitive to the surface of a solid have been developed only over the past ten years, they have been applied to a variety of important technological problems. Nowhere has their impact been more dramatic than in the field of electronic materials and devices. Auger electron, x-ray photoelectron, ion scattering, and secondary ion mass spectroscopies have been applied to all areas of this vast, rapidly growing area. These applications will be surveyed under the general headings of:

- (1) Review of techniques
- (2) General applications to electronic materials and devices
- (3) Effects of analytical techniques
- (4) Silicon
- (5) Germanium
- (6) Compound semiconductors
- (7) Oxide substrates
- (8) Molecular beam epitaxy
- (9) Metallization
- (10) Resistor and capacitor materials
- (11) Interconnections
- (12) Compatibility
- (13) Failure analysis

Specific examples of applications and their impact in each of these areas will be given. These examples will be supported with a complete bibliography of categorized publications.

D-1

Thursday - 1:30 pm

Characterization of Ion Implants in GaAs by AES and GDOS

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The characteristics of many solid state devices fabricated by ion implantation are strongly dependent on the doping profiles produced by the implantation. It is therefore extremely important to develop reliable techniques to determine the implant profiles. To profile the depth distributions of implanted n- and p-type dopants in GaAs, both Auger Electron Spectroscopy (AES) and Glow Discharge Optical Spectroscopy (GDOS) have been successfully employed. The distributions of the implants were examined before and after annealing. In both analyses the depth distributions were profiled by sputtering with inert gas ions and the absolute concentrations were obtained by comparing their signals with those from suitable standards. The experimental results obtained with both AES and GDOS were compared with theoretical ion range statistics and with electrical data. For implantation fluences of 10^{15} - $10^{16}/\text{cm}^2$ and energies of 60-120 keV, the range and magnitude compare favorably with the calculated values. Depth profiles of the samples annealed at temperatures between 700 and 900°C with Si_3N_4 encapsulants in a hydrogen atmosphere exhibited redistribution of the implants by both out- and in-diffusion. Problems in the applications of AES and GDOS to characterize the implant profiles in GaAs will be discussed and the two techniques will be compared.

D-2

Thursday - 2:20 pm

Chemical Corrosion Control for Gold-Plated PCB Connectors. J. S. Murday and E. G. Shafrin, Naval Research Laboratory, Wash., D.C. 20375, and J. D. Guttenplan and L. N. Hashimoto, Rockwell International (Autonetics) Anaheim, CA 92806.

Electrical intermittencies in nuclear submarine navigational computers result from degradation of gold-coated contacts by pollutants accumulating during undersea operation. The resulting insulating films (corrosion, tarnish and organic/sulfide layers) can be removed, but they quickly recur after cleaning. To retard insulating film build-up, a protective, noninsulating chromate treatment was developed for the gold/silver/beryllium-copper connector pins and their mating gold/copper PCB contacts. The treatment has proven effective in extending service life.

Because the protection results from a strictly surface modification, modern surface-sensitive techniques are required for investigating the chromating process. X-ray photoelectron spectroscopy (XPS) shows a thin film ($< 30\text{\AA}$), rich in trivalent chromium. The absence of hexavalent Cr suggests the film acts primarily as a physical impediment to tarnish formation rather than as an electroactive chemical conversion coating. Scanning Auger spectroscopy (SAM) reveals that the microheterogeneity of the contact surface affects film formation. Fixed-beam Auger (AES) shows that chromate deposition and film composition vary in the presence of vestiges of mechanical contact, tarnish growth, etc. The chromating process is chemically complex, and its application in the field is occasionally marred by the deposition of undesirable, insulating films. Analysis of these visibly thick, discolored films by Auger and electron microprobe (EMA) reveals copper to be directly related to the film formation; the localization of Cu to the outermost surface indicates that Cu functions as a promotor of the film formation rather than as an integral constituent of the chromate layer.

D-3

Thursday - 2:40 pm

Ion Scattering Surface Examinations of Calcium
Fluoride Laser Window Materials*

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and

Gene R. Sparrow
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Helium ions scattered from cleaved, freshly cut, polished, and powdered calcium fluoride to assess the utility of ion scattering spectroscopy (ISS) in understanding the structure of fluoride surfaces. It was found that ISS spectra from calcium fluoride surfaces could be obtained provided the surface positive charge buildup is neutralized with electrons. Using 1μ amp/cm² current density of $^4\text{He}^+$ ions at 2.5 keV, the intensity of the fluorine peaks decreased relative to the calcium peak within several minutes of exposing the surface to this ion beam. This decrease is attributed to selective sputtering of the fluorine by the helium ions. However, when the ion beam energy was decreased to 1 keV and a current density of < 300 nA/cm², the intensity ratio of fluorine to calcium remained constant for the duration of the analysis. Scattering intensity data will be presented for various scattering angles from the (111) surface of CaF_2 . The need for using low ion beam energies and current densities, and the needed grazing angle ISS will be discussed in light of the CaF_2 structure. Also, some interesting data on CaF_2 will be shown using $^{20}\text{Ne}^+$ ions. Lastly, the origin of the lattice oxygen peak which was observed in cleaved and polished specimens with ISS and electron spectroscopy for chemical analysis (ESCA) will be discussed.

*Sponsored by Air Force Office of Scientific Research, Contract No. AFOSR-78-3666.

D-4

Thursday - 3:20 pm

SURFACE SILVER ON GOLD ELECTRODEPOSITS

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In connection with the development of selective gold plating processes, ESCA was used to study the surface of gold electrodeposits. High surface concentrations of silver were found on many plated surfaces. Silver correlates with difficulties in thermocompression bonding. It was shown that low levels of silver present in the plating solution are precipitated by metallic gold after plating. A simple method for removing silver in gold solutions was developed and shown to eliminate the problem.

D-5

Thursday - 3:40 pm

A STUDY OF THE OXIDATION OF α AND β BRASS BY
PROMPT NUCLEAR REACTIONS AND RUTHERFORD BACKSCATTERING*

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Brass alloys of two different phases (α , solid solution fcc of Zn in Cu and β , solid solution bcc of Zn in Cu) have been oxidized at different temperatures in pure oxygen ($298\text{K} \leq T \leq 673\text{K}$; $1.3 \cdot 10^3 \text{ Pa} \leq p\text{O}_2 \leq 6 \cdot 10^4 \text{ Pa}$).

In order to analyze the oxide layer in a non-destructive manner, we have used the prompt nuclear reaction $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}$ at 1 MeV and the resonant elastic backscattering (RBS) $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$ for an incident particle energy of 3.05 MeV.

The first method is particularly efficient for evaluating relatively low oxygen concentration (i.e. oxide layers $< 100 \text{ \AA}$). Moreover, since the differential cross section of the nuclear reaction is known accurately no calibration is needed and we can measure without reference to any standard sample. In addition, the high value of the differential cross section of the prompt nuclear reaction at an incident deuteron energy of 1 MeV yields a good detection sensitivity for oxygen near the surface. This technique is also simpler and faster to use. Therefore, most of our results have been obtained in this way, the RBS method serving only to check the accuracy of the procedure. Therewith the influence of the temperature and the phase on the growing of the oxide layer have been studied. Beyond this layer no diffusion of oxygen in the bulk of the sample was noticed for either phase. A crossing point for α and β reactivities versus temperature was found at about 498 K.

These experiments were correlated with the observation by XPS (X-ray photoelectron spectroscopy) of zinc diffusion towards the surface. When increasing the temperature, 473 K must be reached for the β phase, in order that only the zinc signals (Zn 2p, Zn Auger $\text{L}_{3\text{M}_{45}}$, Zn 3p) are still observed, but for the α phase the temperature must go up about 573 K so that the copper signals disappear completely.

Homogeneity of composition in a lateral dimension and morphology of the samples after oxidation were also checked by SEM (scanning electron microscope) coupled with EDAX (energy dispersive analysis of X-ray). It is concluded that, for the range of temperature examined in this work, the heterogeneity is more important in the α phase: areas are found with zinc enrichment differing by ~ 10 percent.

* This work has been partly supported by the IRIS (Institute for the Research in Interface Science) program sponsored by the Belgian Ministry of Science Policy

** Holder of a grant I.R.S.I.A. (Belgium)

ION SCATTERING CHARACTERIZATION OF THE OXIDATION
OF THIN COPPER FILMS ON GOLD SUBSTRATES*

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When a thin film of one metal is deposited on a substrate of another metal and the system is then heated in air or oxygen, compositional changes can occur at both the air/thin film and film/substrate interfaces. In this work, the oxidation and interfacial behavior of a thin copper film/gold foil substrate system were studied by using ISS to obtain in-depth composition profiles of the oxide layer and the overlayer/substrate interface.

The samples used were 20 nm thick copper films deposited on gold foil substrates. Oxidations were carried out in air at 140°C for time periods of 1/2, 1, 3, 6, 13 and 72 h. The ion scattering data were obtained using a static (nonrastered) 1500-eV ^3He ion beam.

To reduce crater edge effects and to obtain a better approximation to the actual composition at the bottom of the advancing crater, an analytic cratering analysis technique was applied to the raw data.

The corrected depth profiles indicated that the Cu/Au interface had become quite diffuse after 1/2 h of heating. As the oxidation continued, it was determined that the interface became increasingly sharper and more distinct.

A model is proposed which assumes that in the initial stages both copper oxidation and copper-gold diffusion can occur simultaneously at the air/film and film/substrate interfaces, respectively. In the later stages, copper first diffuses out of the Cu-Au alloy and then migrates through the oxide layer to complete the formation of the oxide at the surface. Thus, a final two-layer system of $\text{CuO}_{0.67}$ and Au is formed with a sharp interface.

*Most of this work was carried out at Clarkson College, Potsdam, NY

D-7

Thursday - 4:20 pm

On the Rate Controlling Step of Copper
Diffusion/Oxidation Through Gold

by

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In an experiment to determine defect path diffusion parameters, it is important to understand which step is rate limiting. In this work we consider both diffusion of copper through gold via grain boundaries and oxidation (or other surface reaction) and the factors which cause one or the other to be rate limiting. Recently, rate parameters for diffusion and for oxidation have been measured independently.^{1,2} From this published data we conclude that, when the surface reaction is oxidation in clean air, after a few hundred seconds the rate limiting step is oxidation. A second example is given where diffusion is clearly the rate limiting step. In general the factors which determine the rate limiting step are discussed.

¹ H. G. Tompkins and M. R. Pinnel, J. Appl. Phys., 47, 304 (1976).

² M. R. Pinnel, H. G. Tompkins and D. E. Heath, Applications of Surface Science, in press.

D-8

Thursday - 4:40 pm

RECENT PROGRESS IN QUANTIFICATION OF
SURFACE ANALYSIS TECHNIQUES

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A review will be presented of recent developments in the quantification of the four techniques in common use for surface analysis, Auger-electron spectroscopy, x-ray photoelectron spectroscopy or ESCA, secondary-ion mass spectroscopy, and ion-scattering spectroscopy. Particular attention will be given to the following topics:

- (1) The physical structure and compositional homogeneity of a sample. Inhomogeneities in the sample in the region probed by a particular technique set a natural limit to the accuracy and validity of the surface-analysis measurement.
- (2) The Analytical Method. All four analytical techniques can use quantification methods based on standards, sensitivity factors, and a physical model. Comments will be made on the validity and utility of these approaches and on the accuracy of the available data base for the necessary parameters.
- (3) Intensity Measurement. The accuracy of any surface analysis depends a great deal on the extent to which interferences can be minimized and intensities of other processes can be subtracted.
- (4) Instrument Response. Selected results of recent round-robins will be shown to indicate the variability in response from instrument to instrument.
- (5) Practical Considerations. Tradeoffs have to be made between (a) the accuracy and precision of a surface analysis, (b) spatial resolution, and (c) beam damage to the sample.
- (6) Computerization. A growing number of installations use computer systems for processing of measured spectra but the analyst needs to ensure that the obvious advantages are not offset by intrinsic limitations and the external factors described above.

E-1

Friday - 9:00 am

Effect of Surface Plasmon Excitation on
Aluminum Oxide Thickness Calculations in $\text{Al/Cu}_2\text{O}$
Thermite Applications*

by

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and

P. S. Wang and L. D. Haws
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Miamisburg, Ohio 45342

Thermite is a name given to a mixture of powdered metal whose oxide possesses a high heat of formation and a metal oxide of much lower heat of formation that is easily reduced. The thermite under examination is a powdered mixture of aluminum metal and cuprous oxide in a mole ratio of 2:3. The surface chemistry of the powdered aluminum and the thermite mixture was examined by the surface analysis techniques of X-ray photoelectron spectroscopy (XPS) and high resolution Auger electron spectroscopy (AES). Surface characterization with XPS and AES found the presence of carbon and aluminum oxide on the aluminum reactant and mixtures. Surface carbon and oxide thicknesses were calculated from the exponential relationship involving intensity (I), thickness (x) and mean free path (λ) $dI/dx \propto \exp(-x/\lambda)$. The major sources of error in calculating thicknesses from surface measurements will be discussed. These include: photon flux stability, intensity measurements, mean free path, angular detection, interface structure, surface roughness, and surface plasmon excitation. All sources of error will be examined; however, the effect of plasmon excitation will be addressed in detail, especially in regards to oxide thicknesses on aluminum metal.

*Sponsored by Monsanto Research Corporation, Mound Facility, Miamisburg, Ohio 45342.

⁺Senior Engineer with Northrop Corporation, Des Plaines, Ill.

E-2

Friday - 9:50 am

54

Surface Studies by Photoemission of the
Laves-Phases UAl_2 and UCo_2

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Photoemission studies on Laves-phases UAl_2 and UCo_2 have been performed by use of UPS (HeI ; 21.2 eV; $HeII_{\alpha}$; 40.8 eV; $HeII_{\beta}$; 48.4 eV) and XPS (AlK_{α} ; 1486.6 eV). Different "in-situ" surface preparation techniques like scraping, sputtering and heat annealing have been used showing that sputtering changes essentially the surface composition of UAl_2 ; the same effect, but not as pronounced, is found for UCo_2 . Heat annealing restores the initial composition but induces a strong increase of oxygen surface contamination even under UHV-conditions. Scraping in combination with sputtering has proven to be the best surface cleaning procedure. The influence of oxygen surface contamination has been investigated by examining U, Al, Co, O and C core levels (XPS) and the valence band region (UPS/XPS). A typical increase of shifted oxygen induced core levels is observed, whereas the bulk levels disappear. For UAl_2 , the $U4f$ doublet shows for clean scraped material a satellite doublet which is discussed in terms of valence fluctuations of the U-atom and "shake-up" processes. The UPS valence spectra show a superimposition of a spectrum which is very similar to UO_2 spectra and the bulk intermetallic spectrum. An energy shift of the superimposed UO_x spectrum is found to be dependent on the type of the intermetallic compound.

E-3

Friday - 10:10 am

AES Studies of the Influence of Vacuum and
Hydrogen Annealing on the Surface Composition
of 2-1/4 Cr - 1 Mo (ASTM A542) Steel

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Changes in the surface composition of 2-1/4 Cr-1 Mo (ASTM A542) steel as a result of annealing in vacuo ($P < 6.7 \times 10^{-7}$ Pa) and in an ultra-pure hydrogen atmosphere (P_{H_2} approximately 1.3×10^5 Pa) were studied by Auger electron spectroscopy (AES). Ion etched specimens of the alloy were annealed at temperatures ranging from 300 K to 700 K in hydrogen and 300 K to 1000 K in vacuo. The hydrogen anneal treatments were carried out in a separate reaction chamber. The specimens were transferred between this chamber and the AES spectrometer, without being exposed to atmosphere, by means of a vacuum interlock. Comparison of AES spectra taken from hydrogen and vacuum annealed specimens shows that the H_2 atmosphere greatly enhances the segregation of sulfur to the alloy surface.

E-4

Friday - 11:10 am

A Study of Oxide Composition
and Corrosion Susceptibility
of a Heat Treated Fe - Cr
Alloy Using Auger Electron
Spectroscopy

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An investigation was made using Auger Electron Spectroscopy to determine the oxide type and composition of a number of Fe - Cr alloys heat treated at different temperatures and pressures. The MVV transitions of Fe and Cr are related to the oxide type as compared with Fe and Cr oxide reference standards (FeO, Fe₂O₃, and Cr₂O₃). The LMM transitions of Fe and Cr were monitored and compositions were calculated using the elemental sensitivity factors as published by Palmberg. These oxide types were then categorized as far as their corrosion resistance using the anodic polarization curve.

E-5

Friday - 11:30 am

57

Studies of Oxide Films on Iron-Nickel Alloy 52 Using AES*

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and

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The composition of oxide layers and the extent of oxide formation on alloys are of considerable interest. Previous studies on alloys using AES have been useful in showing preferential oxidation following various passivation treatments. In this study, Auger electron spectroscopy was used to characterize the surface composition and the oxide thickness for electrolytically polished iron-nickel alloy 52 specimens that had been given one of the following surface treatments: (1) ultrasonic cleaning in an organic solvent, (2) cleaning in argon plasma, (3) oxidation in boiling 15% H_2O_2 , and (4) oxidation in O_2 plasma. The results show that the oxide increased in the following order: solvent cleaned < oxidation with H_2O_2 < oxidation in O_2 plasma. Also, samples with thick oxides showed the least propensity for atmospheric hydrocarbon build-up. These studies will be discussed in terms of thermodynamic and transport properties of transition metal oxides.

*Sponsored by Monsanto Research Corporation, Mound Facility,
Miamisburg, Ohio 45342

E-6

Friday - 11:50 am

The Use of Bremsstrahlung Radiation to Produce Auger
Lines Inaccessible to MgK α and AlK α X-rays

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It is well established that the binding energy shifts observed in ESCA for chemical compounds differ for x-ray excited Auger and direct photoionized lines. Often the binding energy shifts for Auger lines are greater than the photoelectron lines. The difference in energy between the photoelectron and Auger lines (the Auger parameter) may be used to make chemical identification of many compounds which would be difficult when looking at just the shifts in photoelectron lines. Many very useful Auger transitions require more energy than is produced by conventional MgK α and AlK α x-rays. One way to extend this energy range is to use the bremsstrahlung continuum associated with the principal x-ray lines to excite high energy Auger lines. The intensity of the bremsstrahlung radiation is much weaker than the main x-ray line, but a useable intensity exists to generate Auger lines which possess negative binding energies. In this portion of the energy spectrum, the background is also low. The KLL transitions for Al through Cl lie in this energy range and are particularly sharp making them excellent candidates for determining Auger parameters. We have measured the Auger lines for a number of different compounds containing Al, Si, P and S. We will discuss the expected binding energy shifts, energy resolution and signal-to-background ratios for these Auger lines. Some examples of high energy LMM and MNN transitions will also be discussed. These lines, however, are broader and weaker than the KLL series. In conclusion, we have found for many applications that by measuring binding energies for both the photoelectron line and the Auger line greatly improves ones ability to determine chemical states by ESCA.

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F-1

Friday - 1:30 pm

The Use of Energy Dispersive X-Ray Spectrometry in Conjunction
with Auger Electron Spectrometry for Surface and Thin Film Analysis

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and

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It has been known for many years that the process of generation of Auger electrons is accompanied by the generation of characteristic x-rays. The fraction of hole de-excitations which result in x-ray emission as opposed to Auger electron emission, for a particular hole, is known as the fluorescence yield. Because fluorescence yields are typically small for the transitions most often used in Auger Electron Spectroscopy (AES) the concurrently produced x-rays have not been viewed as a significant source of additional information. However, with the advent of high efficiency, thin window energy dispersive x-ray detectors it is possible to extract valuable additional information from the x-ray spectrum. Comparisons with Auger spectra have indicated a detection limit for C and O which is within a factor of 10 of the detection limit of a standard Auger spectrometer. The larger sampling depth for the x-rays has been another reason to question their utility in surface analysis but this can also be used as an advantage. One of the least defined areas in AES is the depth-scale calibration in depth profiles. For films whose thickness is less than the x-ray sampling depth the absolute removal rate can be measured from the rate of change of the x-ray signal intensity from any of the components of the film. The use of this technique has identified variations in removal rate of nearly an order of magnitude during the profiling of GaAs oxides on GaAs. Examples of the effect of this new information on depth calibrations will be presented, from the GaAs oxide system and others.

F-2

Friday - 1:50 pm

60

Electron Spectroscopy of $\text{TiD}_{0.9}$ and TiH_x Surfaces

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and

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Metal hydrogen systems promise immediate or potential applications in such areas as hydrogen embrittlement, powder metallurgy, hydrogen storage and electrodes for fuel cells. For such uses, the Ti-H system is particularly promising because of the extremely high absorptive densities attainable.

The electron spectroscopic effects of different interstitial densities of hydrogen and deuterium were investigated by Auger electron spectroscopy (AES), electron loss spectroscopy (ELS) and x-ray photoelectron spectroscopy (XPS). The plasmon energy shifts, determined by ELS, are shown to vary linearly with increasing hybridization, suggesting the free-electron nature of the electrons added by hydrogen or deuterium. The magnitude of the Ti_{2p} XPS shifts varied linearly with hydrogen concentration, and suggested anionic hydrogen. Valence band spectra of TiH_x samples showed development of a new feature 5-7eV from the Fermi level as x was increased. The valence band spectra are consistent with the recent band structure calculations, and new AES features of titanium hydrides can be interpreted as convolutions with the valence band.

F-3

Friday - 2:10 pm

61

R. Gerald Keil, Ph.D.
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Paper Entitled "The Formation Of Thin Uniform
Insulating Films For Inelastic Electron
Tunneling Spectroscopy"

In 1966, Jaklevic and Lambe discovered a new spectroscopic technique which has come to be known as inelastic electron tunneling spectroscopy (IETS). In this technique, the vibrational modes of molecules are probed by electrons which tunnel through a thin insulating barrier containing those molecular species. Both Raman and infrared excitations can occur during the passage of the electron in the vicinity of the molecule. The tunnel junctions studied in IETS have a characteristic metal-insulator-metal sandwich structure where the metals are 500 to 3,000 Å in thickness while the insulator is much thinner, only 30 Å. Not surprisingly, such structures are fragile. The insulator used to separate the metals is usually an oxide of one of the metals, usually aluminum, formed by glow discharge in an oxygen environment. This technique does not result in the regular formation of satisfactory junctions. The major obstacle to the preparation of suitable barriers is shorting of the junction by metallic bridges connecting the electrodes. Because the insulating layer is necessarily thin, defects such as pinholes, are likely and frequently produce shorts.

The use of alternative methods of generating the requisite insulating film will be discussed. Liquid phase anodization using both galvanostatic and potentiostatic techniques result in the formation of resistive oxide layers on aluminum where the film thickness (resistance) can be readily controlled. By comparison, liquid phase anodization is preferable to the gas phase glow discharge technique because of its reliability factor. Results using these methods will be presented.

F-4

Friday - 2:30 pm

SECTION V
WORKSHOP CONCLUSIONS

A survey was conducted during the Workshop to find out attendees' views on (a) Workshop organization, (b) the quality and variety of the papers, (c) whether or not the Workshop filled a need, and (d) if future Workshops are held, should they be annual or biannual? Forty-seven survey forms were completed and handed in with the following results:

Workshop organization	Good	41
	Poor	0
Quality of papers	Good	33
	Poor	1
Variety of papers	Good	33
	Poor	1
Was a need filled?	Yes	40
	No	2
Future Workshop	Annual	33
	Biannual	11

Other comments written on the survey forms included:

(a) surface scientists should be organized into a national society, with the Workshop being a small beginning,

(b) there should be a stronger attendance by industrial laboratories, perhaps encouraged by invited speakers from industry,

(c) laboratory visits would be desirable,

(d) non-vacuum papers (Raman spectroscopy and photoacoustic spectroscopy) were intriguing, and

(e) such a concentration on surface analysis techniques and results is not available elsewhere.

Because of the very positive response by the attendees, it is concluded that similar Workshops should be held in the future. The University of Dayton would be willing to organize such future Workshops and to make their facilities available for them.